



ontario hydro research division

EXECUTIVE SUMMARY

DECONTAMINATION OF PICKERING NGS FUELING MACHINE OIL

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Recent work on the conditioning requirements for tritiated waste oils arising from the Darlington Tritium Removal Facility demonstrated that tritium contamination as either gas or tritiated water causes tritiation of the oil and its additives. The degree to which this occurs is apparently a function of the tritium concentration and exposure time to tritium. Consequently tritium releases from these oils cannot be explained simply on the basis of tritium gas or tritiated water behaviour.

A recent report from RMEP on the proposed clean up of tritiated oil at Pickering assumed that the oil could be effectively decontaminated by removing the dissolved and suspended water in the oil because tritiated water was the original contaminant. This was contrary to our earlier findings. In view of this the proposed vacuum degassing scheme was simulated under laboratory conditions primarily to confirm the validity of our previous findings but also to point the way to more efficient tritium removal processes.

The work reported here confirmed our earlier conclusions that while tritiated water is the major contaminant, it tritiates other polar species in the oil which are less volatile. Techniques such as vacuum degassing while efficient for the removal of water are very slow for the removal of the tritium containing contaminants requiring at least 7 days under vacuum to reduce tritium concentrations by a factor of 10. Other processes such as water washing, paper filtration and filtration through a number of absorbents all were able to achieve decontamination factors equivalent to vacuum degassing but more rapidly. However, of the materials tested, only an absorbing material composed of a magnesium oxide/silicon oxide co-precipitate was able to reduce the tritium activity to less than 10 uCi/L, the level below which the oil can be considered to be non-radioactive.



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To: Dr.D. Mills
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DECONTAMINATION OF PICKERING NGS FUELING MACHINE OIL

J.P.Krasznai

Laboratory scale tritium decontamination tests have been carried out on Pickering F/M oil. The objective was to test the assumption that the predominant tritiated species in the oil was water and could be removed by vacuum degassing. The work reported here shows that while tritiated water is the major contaminant, it tritiates other polar species in the oil which are less volatile. The tritium decontamination of oil by vacuum degassing is a slow inefficient process. Other processes such as water washing, paper filtration and filtration through a number of absorbents all were able to achieve decontamination factors equivalent to vacuum degassing but more rapidly. However, of the materials tested, only an absorbing material composed of a magnesium oxide/silicon oxide co-precipitate was able to reduce the tritium activity to less than 10uCi/L, the level below which the oil can be considered to be non-radioactive.

INTRODUCTION

The Pickering fueling machines are controlled hydraulically and normal leakage of this oil into the F/M service room sump results in its contamination by tritiated heavy water and radioactive particulates. This waste oil is separated from the heavy water and stored at the station. There is currently 180,000 liters in storage at site and is accumulating at a rate of 400 L/week /1/.

RMEP has proposed/1/ that the old oil that has accumulated be decontaminated using commercially available processing equipment and subsequently released to commercial waste oil recycling companies and disposed of as if it were non radioactive.

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In the work on tritiated waste conditioning for liquid wastes arising from the Darlington Tritium Removal Facility (TRF) it was found/2/ that oil exposed to tritium gas incorporated tritium into the hydrocarbon structure and formed a wide range of organic tritiated species. This phenomenon which is caused by the radiolytic formation of hydrocarbon radicals and subsequent polymerization of these radical species, is responsible for the increased viscosity of oil exposed to tritium gas. In view of the high solubility of tritium gas in oil (% quantities) compared to tritiated water (ppm quantities) the incorporation of tritium into hydrocarbons in oil exposed to tritiated water is likely to be relatively small and be somewhat dependent on the composition of the oil, its tritium content and the length of exposure to tritiated water. Turbine oils, however, contain/3/ antioxidants and corrosion inhibitors which are polar, oil soluble compounds such as para tertiary butyl cresol and alkali metal soaps. These compounds and their degradation products are likely to incorporate tritium more readily than the oil itself.

In view of the desire to dispose of the Pickering F/M oil after clean up as non radioactive, we attempted to duplicate the conditions of the proposed oil clean up system to determine the validity of the assumption /1/ that by reducing the water content of the oil the tritium content is correspondingly reduced.

This report details the work on the tritium decontamination of oil by vacuum dehydration. Some preliminary work on alternative tritium removal methods is also reported.

EXPERIMENTAL

Two types of oil were used in these experiments:

(1) Teresso 32, a turbine lubricating oil, was contaminated with high Curie moderator water. The exposure time was of the order of 2 years at a specific activity of 2.1uCi/mL oil.

(2) Teresso 46, also a turbine lubricating oil, which is used as a hydraulic oil in the Pickering fueling machines. A sample of this oil was obtained from Pickering Operations for this work. The oil was taken from a drum and from its apparent cleanliness was assumed to be relatively new oil. The tritium activity in the oil was 0.46uCi/mL. The length of exposure of this oil to tritium is not known.

The vacuum distillation unit consisted of a conical Pyrex flask fitted with a septum through which oil could be added or removed by means of a syringe. A short length of vacuum hose connected this flask to a pump capable of 7 kPa (1 psia) vacuum.

The oils were fully characterized prior to vacuum distillation with respect to their radionuclide inventory and water content (Table 1).

TABLE 1

Properties of the As-Received Specimens

Oil	Water (mg/kg)	PCB (mg/kg)	Tritium (uCi/L)	C-14 (uCi/L)	Co-60 (nCi/L)	Cs-137 (nCi/L)
Teresso 32	118	-	2100	0	0	0
Teresso 46	133	16	455	7.9	51.9	10.2

Experiment 1.

50 mL Teresso 32 oil was introduced into a flask which was then evacuated at room temperature. Daily samples of oil were withdrawn and analyzed for tritium by both direct liquid scintillation and the combustion/liquid scintillation technique. The latter method involved absorbing a known weight of oil onto cellulose and igniting the mixture in an oxidizer. The tritiated water so produced is then mixed with scintillation cocktail and counted.

After vacuum pumping at 7 kPa for 15 days which was the time required to reach a constant tritium concentration, water equal to three times the volume of oil in the flask was added to the oil and the mixture left stirring at atmospheric pressure and room temperature for 72 hours. The water/oil mixture was subsequently allowed to separate and the water layer removed and analyzed for tritium. The oil was further pumped under vacuum at a pressure of 3 Pa (4×10^{-4} psia) until the tritium concentration was constant.

Experiment 2.

These conditions however were not truly representative of the vacuum degassifier commercially available. In view of this a means to increase the surface area of the oil droplets as they enter the vacuum chamber was included in our set up. This was done by heating the oil to between 40°C-50°C and drawing it through a glass frit into the receiving flask which was under vacuum. As the oil moves through the frit it foams, the surface area of the oil droplets is increased thereby increasing the effectiveness of the dehydration process. Both water and tritium in the samples were analysed periodically for the duration of the experiment.

Water content determinations were carried out using the Karl-Fisher titration method on a Metrohm Coulometer KF instrument.

Experiment 3.

In this experiment both a sample of the as received Pickering oil and one from which most of the water and tritium had been removed by vacuum degassing were passed separately through a Florisil column. This material is a strongly acidic absorbent consisting of a magnesium oxide silicon oxide co-precipitate/4/. It is used to remove polar contaminants from oils prior to chromatographic analysis for PCBs in oil.

Experiment 4.

Samples of both as received oil and oil from which most of the water and 90% of the tritium had been removed were passed through or mixed with a number of other polar absorbents and the tritium decontamination factor determined.

Experiment 5.

In this experiment, as-received oil was washed with three times its own volume of water and also water to which a non-ionic emulsifier, Triton X114 was added in order to facilitate the washing process. Following the washing the oil/water mixture was allowed to separate and the tritium concentration in each phase was determined. The oil layer was subsequently vacuum degassed at 4 Pa (6×10^{-4} psi), and the tritium concentration redetermined.

RESULTS AND DISCUSSION

Table 1 summarises the characteristics of the two oils. The two types of oil were individually vacuum degassed at room temperature and the tritium concentration determined daily. Figures 1 and 2 show how the tritium concentration varied with time. The tritium concentration decreased rapidly. In the first 24 hours two thirds of the initial tritium inventory had been removed from both types of oil (3% per hour). Subsequently the removal of tritium by removing volatiles was slow (<1% per day). Even washing the oil with an excess of water for 4 days followed by further vacuum distillation at a lower pressure or heating to 40°C did not reduce the tritium concentration further. It is interesting to note that the residual tritium activity after vacuum distillation expressed as a percentage of the initial inventory was similar for both oils ie 7-10%.

FIGURE 1

Vacuum distillation of Tritiated Hydraulic Oil at 7 kPa

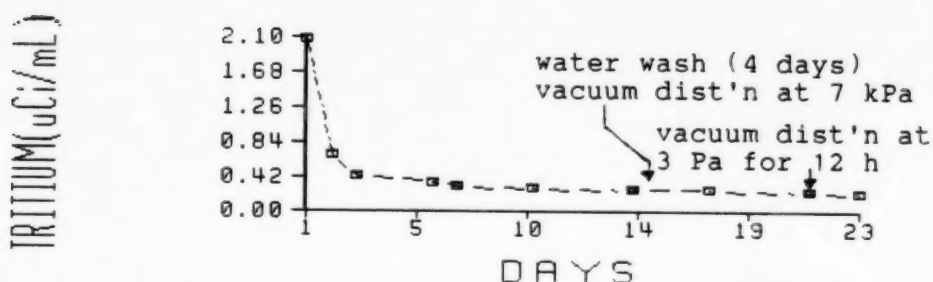
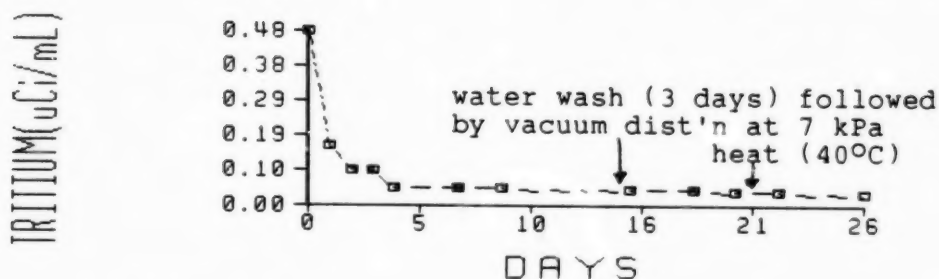


FIGURE 2

Vacuum Distillation of Tritiated Pickering NGS F/M Oil at 7 kPa



The absolute tritium concentration following vacuum degassing, however, was significantly greater in the oil which had the highest tritium concentration initially. In neither case however was it possible to reduce the tritium concentration below 35uCi/L by simple vacuum distillation. In fact the results suggest that the final tritium concentration achievable by vacuum distillation is dependent on the initial tritium activity. The C-14 concentration in the oil following vacuum distillation was reduced by a factor of 27 to 0.3uCi/L. This indicates that the

C-14 contamination is not in particulate form but most probably exists as an equilibrium mixture of dissolved CO₂ and carbonate/bicarbonate ions.

This initial experimental set up was not representative of the vacuum degassing equipment purchased/4/ for the clean up of the Pickering oil. In this equipment oil is forced through a heater element and an atomizer into the vacuum chamber which is at a pressure of 4 torr (0.5kPa). To simulate these conditions in the laboratory the oil was first heated to 50°C and then drawn into the vacuum flask through a sintered glass frit to increase the surface area of the oil droplets. This process was repeated three times to simulate recirculation of the oil through the atomizer into the vacuum chamber. The results of two experiments, one at room temperature (Expt 2a) the other at 50°C (Expt 2b) are shown in Table 2. The tritium activity in the oil is expressed as the amount of tritium in uCi per unit volume of oil. The tritium activity in the oil can also be expressed as a specific activity of tritium in uCi per unit volume of water which is contained in the oil. The specific activity of tritium in oil can be mathematically stated as:

$$\text{Specific Activity} = \frac{\text{Tritium Activity in oil (uCi/mL)}}{\text{Water content of oil (mg/kg oil)}}$$

The specific activity is calculated in the last two columns of Table 2.

Table 2

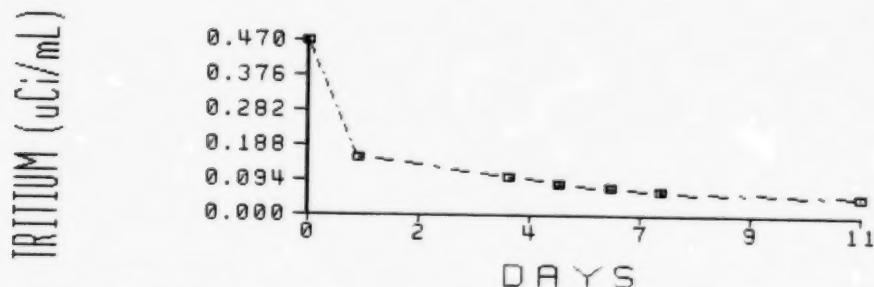
Cycle #	<u>Tritium in Oil (uCi/mL)</u>		<u>Water (mg/kg)</u>		<u>Sp. Act. (Ci/L)</u>	
	Expt 2a	Expt 2b	Expt 2a	Expt 2b	Expt 2a	Expt 2b
0	0.427	0.468	84	51	5.5	10.2
1	0.388	0.424	43	35	10.0	13.5
2	0.299	0.374	17	15	19.5	27.7
3	0.296	-	14	-	23.5	-

Cycle 0 represents the initial conditions just prior to vacuum distillation, and the duration of the three cycles was of the order of 1-2 minutes. It is apparent that the tritium concentration decreases much more slowly than the water content which results in an increase in the specific activity of tritium in the water remaining in the oil. If the tritium was associated exclusively with water then the specific activity of tritium would be expected to remain constant as water is removed from the oil during vacuum degassing. The fact that this is not observed indicates that the tritium carrying species is not water but a

less volatile compound suspended or dissolved in the oil. Further pumping the stirred oil at 4 Pa for 11 days (Figure 3) resulted in a tritium concentration in the oil of 54uCi/L, which represents a decontamination factor of 9, consistent with the data from the first set of experiments.

FIGURE 3

Vacuum Distillation of Pickering NGS F/M Oil (4 Pa)



The oil remaining after the vacuum distillation was subsequently passed through the glass frit into the vacuum chamber through six cycles. Neither the water content nor the tritium concentration changed significantly.

A sample of this detritiated oil and the as-received material were passed through Florisil columns, which strongly absorb polar molecules, using iso-octane as the carrier. The tritium was reduced to background levels in both samples (Table 4), confirming the earlier suggestion that the tritium carrying species are polar components associated with oil. On this basis it should be possible to drive the tritium by isotopic exchange into the water phase by washing the oil with an excess of water. In the earlier experiments this was tried after most of the tritium had been removed from the oil but without any success. The experiment was repeated using as-received oil which was mixed with three times its weight of water for 3 days. A duplicate sample using some Triton X114 surfactant to increase the oil droplet surface area was also prepared. The water and oil phases were separated by adding salt and centrifuging and the tritium concentration in both phases was then determined. The results, Table 3, show that the tritium concentration was reduced in the oil phase by a DF of 7. The tritium in the water layer increased to 0.157uCi/mL which was 30% greater than expected based on a tritium balance between the two phases. The water layer was not clear and probably contained suspended oil causing the tritium activity in the water layer to be higher than expected. In the

sample containing the surfactant the tritium content of the water layer was similar and therefore the presence of a surfactant was not beneficial.

Table 3

Sample	Mass(g)	³ H in Oil(uCi/mL)		³ H in Water(uCi/mL)	
		<u>Before</u>	<u>After</u>	<u>Before</u>	<u>After</u>
<u>1</u>					
Wt. Oil	17.84				
Wt. Water	55.67	0.355	0.052	0	0.157
Wt. Triton X-114	-				
<u>2</u>					
Wt. Oil	17.44				
Wt. Water	55.14	0.355	0.057	0	0.129
Wt. Triton X-114	2.1				

The evidence from all of the foregoing experiments is clear. The tritium activity remaining in the oil after vacuum distillation or water washing is associated with species which are polar as shown by the complete absorption of the tritiated species on a Florisil column. However, it would appear that the tritium is not part of the polar group since it does not exchange with water. Removal of this residual activity therefore requires its absorption by materials which are specific polar absorbents such as clays and oxides of aluminum, magnesium and silicon. Table 4 shows the results from a few tests on some readily available absorbents. Florisil, a magnesium oxide silicon oxide co-precipitate was the best but it is not available on an industrial scale and furthermore its capacity is low. Silica gel was the next best absorbent and warrants further investigation to determine its capacity and optimum operating conditions either as a polisher after a vacuum degassifier or as a decontamination system by itself.

Table 4

<u>Absorbent</u>	<u>Mass Fraction</u>	<u>Tritium Conc'n (uCi/mL)</u>		<u>D.F</u>
		<u>Before</u>	<u>After</u>	
Florisil	0.02	0.349	Bkg.	
		0.054	Bkg.	
Alumina	0.10	0.292	0.022	13.3
Silica Gel	0.50	0.292	0.015	19.5
Fuller's Earth	0.05	0.349	0.038	9.2
		0.054	0.021	2.6
Paper Filter	-	0.540	0.053	10.2

The flowsheet for the clean-up of the Pickering oil will include a piece of equipment called the Mobile Oil Filtration Unit. This system which is downstream of the vacuum degassifier, utilizes a two stage filter consisting of a pleated paper filter cartridge and a charged filter cartridge to remove particles in the 0.02um-1um range. In this work materials associated with the MOFU system were not tested for residual tritium removal nevertheless it is the opinion of RMEP/6/ that the system will function effectively to reduce tritium in the oil to the level at which it can be disposed of by commercial outfits.

CONCLUSIONS

Oil which has been mixed with tritiated water forms a mixture in which the predominant tritium carrying species is polar but it is not water. The assumption that the oil can be completely decontaminated by removing the suspended and dissolved water is not valid.

Vacuum distillation will result in a removal of both the water in the oil and the tritium carrying species which is volatile but less so than water. This technique however, while efficient for the removal of water is very slow for the removal of the tritiated materials. Furthermore vacuum distillation is unable to reduce the tritium activity below 50uCi/L which is five times the concentration at which the oil is considered to be non-radioactive.

Washing the oil with water will transfer close to 85% of the contained tritium activity into the water layer. The remaining 15% however cannot be removed by vacuum distillation.

In order to reduce further the tritium activity in the oil, passing the oil through a medium capable of absorbing polar species is necessary. In this work, Florisil, a co-precipitate of magnesium and silicon oxide was found to be an excellent material, reducing the tritium activity to background levels. Silica gel which is more readily available is also a promising material although it is less efficient.

Conversations with filter suppliers and research personnel familiar with filtration indicate that although the charged filter system might remove some of the tritiated species the efficiency of this process is largely an unknown given that the filter is designed to remove particulates and not act as an absorbent.

From these experiments it would appear that the degree of decontamination of the oil depends on how much tritium activity is originally present in the oil. Only one oil sample was used in all of these experiments, and the conclusions reached here are based on one sample. While they are consistent with our earlier

work on tritiated oils, a strategy for oil clean up at Pickering should ensure that whatever oil is presently in storage is well characterized.

The rationale for the work reported here was to validate an assumption because it was contrary to conclusions reached in our earlier research work on tritiated waste oil conditioning. The intent was not to change the processing plan for the oil clean up at Pickering. However in the course of this work some valuable information was obtained which suggests that:

- (a) removal of tritium to very low levels is much more difficult than originally assumed, and with the proposed equipment tritium levels of 10uCi/L are unlikely to be achieved.
- (b) the original clean-up scheme is not the best and can be simplified.

RECOMMENDATIONS

- (1) Since vacuum degassing as a technique to reduce tritium concentration in oil is a slow process which will result in a residual tritium activity >10uCi/L, its use for the processing of the large volume of oil at Pickering is questionable. Tritium decontamination factors of 7-10 can be achieved more rapidly by simple water washing, paper filtration or using clays such as Fuller's earth.
- (2) The ability of the Mobile Oil Filtration System as a polisher to reduce tritium concentrations to the required 10uCi/L level is also questionable and should be confirmed, preferably in the field on the actual unit which will be used for the processing.
- (3) The effectiveness of decontamination of tritiated oil may be dependent on the age of the oil and the degree of tritium contamination. If decontamination to "de minimis" levels is a continuing objective, then more samples of the oils should be characterized with respect to their tritium, water and PCB content.

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